THE CONVERSION OF COAL TO ACETYLENE IN ARC HEATED HYDROGEN

R.E. Gannon, V.J. Krukonis, T. Schoenberg

AVCO Corporation/ATD
Lowell Industrial Park
Lowell, Massachusetts 01851

I. INTRODUCTION

In recent years intense research has been directed toward the development of coal treating processes designed to produce hydrocarbons for the chemical industry. The major portion of this effort has been aimed at producing pipeline gas and coal-derived liquid fuels, such as gasoline, by processes involving high pressure, catalytic hydrogenation carried out in fluid bed (1), slurry (2,3) and transport reactors (4).

While the processes for producing gaseous and liquid fuels by conventional techniques were being developed, exploratory experiments to investigate the rapid pyrolysis of coal to gaseous products were in progress. In these studies energy sources such as d.c. arcs (5,6), lasers (7), flash lamps (8), plasma jets (9-12) and arc image furnaces (13,14) have been used to heat coal at temperatures above 1500°C. The results of these studies show that the rapid pyrolysis of coal produces a gaseous mixture of which acetylene is the principal hydrocarbon constituent. These results are consistent with the free energy data of Wagman, et al (15) and Howard, et al (16) (Figure 1) which show that at ordinary temperature the paraffinic and olefinic hydrocarbons are more stable than acetylene, but with increasing temperature the free energies of these hydrocarbons become progressively more positive until at temperatures above 1200°C they are less stable than acetylene. In gaseous mixtures above 1200°C, therefore, acetylene should be the predominant species. Upon cooling the mixture, however, much of the acetylene is lost as it becomes more unstable toward its elements as well as toward other hydrocarbons. The fact that acetylene is identified in the cooled gas mixture, however, indicates that the rate of the formation is greater than the rate of the decomposition reactions. From these considerations it is obvious that to produce appreciable quantities of acetylene it is necessary to heat the reactor mixture to temperature above 1200°C to obtain a mixture rich in acetylene and then to quench this mixture rapidly in order to preserve as much of the acetylene as possible. Features of a plasma jet reactor which allow the reaction mixture to be heated to approximately 2000°C and rapidly cooled to ambient conditions in a matter of milliseconds obviously exhibits potential as a reactor for the conversion of coal or other hydrocarbons to acetylene.

II. EXPERIMENTAL

A. APPARATUS

The work described in this paper is concerned with the formation of acetylene through the exposure of coal to hydrogen which has been heated by passing it through an electric discharge. The basis for this technique was demonstrated by previous workers (9, 10, 11) who showed that acetylene could be produced by heating coal in an argon plasma jet. It was further shown that the acetylene formation could be enhanced by including small amounts of hydrogen in the argon stream. Each group of workers, however, was limited to hydrogen concentrations below 30% by the severe erosion of the electrodes of the plasma generator when operated at higher hydrogen fractions.

At AVCO it was found that a plasma generator equipped with a tungsten-tipped cathode and a water-cooled copper anode could be operated using pure hydrogen gas without measurable erosion of the electrodes. This unit was therefore adapted to a reactor chamber which would allow the introduction of coal directly into the plasma jet followed by immediate cooling to room temperature in a water-cooled chamber and water-cooled exit pipes. A schematic drawing of the reactor is shown in Figure 2. The plasma generator is a 30 kw unit which when operated with hydrogen is 75% efficient, i.e., 75% of the electric energy is converted to gas enthalpy. This was determined by measuring the energy absorbed by cooling water circulated around the electrodes. Similiarly it was determined that when operated with argon it was only 50 to 55% efficient.

To obtain an estimate of the reaction temperature and temperature profiles, provision for measuring the temperature at twenty four stations within the reactor were made. Tungsten-5% rhenium, tungsten-26% rhenium thermocouples from the nozzle, viz., 3/4", $1\frac{1}{4}$" and 1 3/4 ". These thermocouples and housings provided the capability for measuring temperatures up to 5000°F. The millivolt output of the thermocouples was fed to a multiposition recorder so that the time-temperature history at each of the three vertical positions could be obtained simultaneously. The radial temperature distribution was obtained by eight measurements made at $\frac{1}{4}$" intervals from the centerline of the reactor at each of the three vertical distances. Figure 3 shows the measured temperature profile in the reactor at distances of up to 1 3/4" from the nozzle. The left side of each curve shown was drawn by symmetry to the measured right side.

For the operating conditions shown on the figure, the temperature of the hydrogen leaving the nozzle was calculated to be 5200°F. The measurements show that this temperature declined to 4100°F at 3/4" from the nozzle and then to 2400°F at $1\frac{1}{4}$" and to 1900°F at 1 3/4". The radial temperature distribution shows a steep gradient at the 3/4" distance but only a slight gradient at 1 3/4" as the jet expands as it progresses away from the nozzle.

Temperature measurements with coal feeding were attempted but could not be extended for more than several seconds because the coal reacted rapidly with the beryllia sheath and then with the tungsten-rhenium thermocouples. When the coal was introduced, the centerline temperatures of the two furthest thermocouples, $1\frac{1}{4}$" and 13/4" from the nozzle, dropped about 500°F before the thermocouples failed. The thermocouples closest to the nozzle, however, did not record a temperature decline indicating that the coal was not reaching the hottest part of the jet.

The coal is fed to the reactor from a 6000 gram hopper by means of a screw feed system. The speed of the screw feeder and consequently the coal feed rate is controlled by a variable speed motor. Hydrogen, typically 2.4 SCFM, is introduced to the coal feed line after the screw feed to act as a carrier gas. The coal-hydrogen mixture is conducted into a circular manifold from which it is injected into the plasma through a series of small holes around the inside diameter, as illustrated in Figure 4. Controlled coal feed rates of between 125 g/min and 550 g/min are possible with this arrangement.

The effluent gases from the coal-hydrogen reaction are sampled by means of a probe in one of the exit lines. Gas chromatography is then used to analyze the collected gases using a Porapak N column and a flame ionization detector to analyze for the hydrocarbons and a silica gel column and a thermal conductivity detector to analyze for H_2, CO, CO_2 and air.

B. RESULTS

In studying the feasibility of producing acetylene by subjecting coal to arc heated hydrogen it is evident that three critical parameters must be measured: 1) the yield of acetylene per pound of coal used 2) the energy required to produce a pound of acetylene 3) the concentration of acetylene in the exit gases. Because each of these parameters should be dependent on the process variables, it is important to designate the operating conditions at which the critical parameters are optimum, i.e., a high yield and concentration and a low specific energy requirement (SER). Considering the process, two variables, the rate of coal feed and the enthalpy of the hydrogen from the arc appear to be of primary importance. For this reason, the three parameters, yield, concentration and SER were studied first as a function of enthalpy at a constant coal feed rate and then as a function of coal feed rate at a constant gas enthalpy.

In the initial runs it was determined that the conversion process was more efficient when the reactor was operated at pressures between 0.2 and 0.5 atmospheres. The subsequent runs were therefore performed under reduced pressure. Pittsburgh Seam Coal, of a -100 + 200 consist was used in all runs in this study.

The results showing the effect of gas enthalpy and coal feed rate on yield, concentration and SER are shown in Figures 5 and 6. For this data, yield is defined as pounds of acetylene produced per pound of coal (including ash and moisture content) introduced, concentration is the moles of acetylene per mole of exit gas and SER is the kilowatt hours of electricity to the system (including losses to the electrodes and walls) required to produce one pound of acetylene.

III. DISCUSSION

The general effect of gas enthalpy on the critical parameters of the process are predictable and consistent with the results shown in Figure 5. That is, it would be expected that the acetylene yield and concentration should increase with increasing enthalpy and that the SER should go through a minimum where enough energy is available to convert the coal to acetylene with a minimum of energy being lost in the exit gases.

In considering the effect of coal feed rate, illustrated in Figure 6, it is predictable that the yield should decrease with increasing coal feed rate. It should also be expected that as the coal feed was increased the average enthalpy of the coal-gas mixture would decrease. Using this reasoning it would be predicted that once the ideal coal feed rate for the fixed gas enthalpy of the test was reached, the concentration should reach a maximum and then decrease as the average enthalpy of the mixture decreased with increasing coal feed. Similiarly it could be predicted that the SER value should go through a minimum as an increasing percentage of the energy is used as sensible heat for the additional coal. These predictions are not substantiated by the data given in Figure 6 as the concentration appears to attain a maximum at a coal feed rate of 130 g/min, and to remain nearly constant to feed rates of over 250 g/min. The SER values behave in a similiar manner, achieving a low value of about 7 kwh/lb. at 130 g. of coal/min. and remaining constant to the maximum coal feeds tested.

The departure from the predicted behavior as the coal feed was increased can be explained on the basis of the competing reactions of forming acetylene at high temperatures on one hand and then allowing it to decompose before it is effectively quenched. To substantiate the premise that appreciable amounts of acetylene decompose before it is quenched a series of experiments to study the rate of acetylene decomposition was performed. In these experiments a gas mixture of 6% acetylene and 94% hydrogen was introduced through the ports where the coal is normally injected. The amount of decomposition of the acetylene was then determined as a function of gas enthalpy. The results, given in

Figure 7, showed that at high gas enthalpy (4.0 kw/SCFM) as much as 36% of the original acetylene decomposed and at 1.8 kw/SCFM, the enthalpy level for the data given in Figure 6 , 16% of the acetylene decomposed. Extrapolation of this data indicates that as the enthalpy is decreased below 1.8 kw/SCFM by the addition of coal, the rate of acetylene decomposition will also decrease. The plateaus in the concentration and SER values shown in Figure 6 can then be intepreted as indicative of a balance in the competing reactions where although less acetylene is formed because of the decrease in average enthalpy (caused by the additional coal) less acetylene is decomposed for the same reason. At some higher coal feed rate, the enthalpy of the mixture will fall below the level required to form 8% acetylene and a corresponding decrease in the final acetylene concentration will be observed.

Since the early work with the argon plasma coal reactions (9-11) Newman and his co-workers (12) at the National Coal Board in England have also adapted a hydrogen plasma jet to produce acetylene from coal. The lowest SER value reported in this work corresponds to about 8.5 kwh/hr and was achieved with a gas enthalpy of about 3.0 kw/SCFM at a coal feed rate of 160 g/min. This SER value is appreciably higher than the lowest values given in Figure 5 and comparison of the data suggests that the experiments at the National Coal Board were performed at excessive gas enthalpies. In addition it was shown that the radial coal injector, illustrated in Figure 4, distributed the coal more uniformly and consequently more efficiently than a straight tube injector apparently similiar to the one used by Newman et al.Russian workers (17) also developed a hydrogen plasma jet and used it to form acetylene from methane. Their SER values, however, were two to three times higher than those reported in this paper.

Evaluation of the process as a commercial method of producing acetylene can be based on a recent study by the Stone and Webster Engineering Co.(18). This study was designed to evaluate an arc-coal process of producing acetylene in which the coal is injected into the inter-electrode region. The same critical parameters are important in each process and the same mine-mouth operation considered by Stone and Webster can be utilized in the evaluation of the arc heated hydrogen process.

The current price of acetylene depends on the size of the contract, the location and the process. For large contracts acetylene costs about 8¢/lb when produced by the carbide or partial oxidation process. (19) If we select 7¢/lb as a target cost for producing acetylene by the arc heated hydrogen process we can use the Stone and Webster data for designating the combination of operating parameters required to make the process viable. Using a conservative price for electricity of 5.25 mils and considering a 300 million pound per year plant it can be shown that a process in which the yield is 18%, the concentration 12% and the SER value 4.5 kwh/lb, or a case in which the yield was 30%, the concentration 12% and the SER value 5.75 kwh/lb, would meet the target cost. These values are admittedly based on conservative data; that is, no credits other than fuel credits were taken for by-products and it was indicated that electricity costs of about 4.0 mils could be negotiated for an acetylene plant with a load of about 100 mw. If reasonable credits are taken for the chemical value of the by-products and 4.0 mil power is used, a cost reduction of about 1.5 cents per pound could be realized or a process in which the SER value was about 6.5 kwh/lb would be considered viable.

The most promising direction for additional improvements in the process would appear to be toward utilizing the highest temperature portions of the plasma jet to better advantage. As was indicated in the plasma temperature measurements, the coal was not reaching the central portion of the jet and consequently the highest energy gases were not being utilized in the conversion reaction. Better coal penetration may be achieved by feeding a portion of the coal through a hollow cathode or by feeding the coal counter-current to the plasma jet.

Another method in which the reaction of coal with arc heated hydrogen could be utilized to advantage is in combination with the previously cited (6) process in which the coal is injected directly into the arc. In such a process a large portion of the coal is volatilized in the inter-electrode region and the effluent gas mixture consists of acetylene and other hydrocarbon species as well as arc heated hydrogen. Injecting coal into this plasma jet, as shown in Figure 6, should serve to react with the arc heated hydrogen to form additional acetylene, as previously shown, and to quench the high temperature hydrocarbon species to preserve a high percentage of the acetylene. The combination of the two processes would be analogous to the Huels process (20) in which liquid hydrocarbons are injected directly into the arc as well as downstream of the arc. Initial tests in which the combined processes were tried with coal injection showed a 10 to 15% increase in the acetylene concentration with a corresponding decrease in SER values. A decrease in acetylene yield was also noted. This can be traced to the additional coal, added downstream, which apparently isn't converted to acetylene as efficiently as the primary coal charge injected directly into the plasma.

ACKNOWLEDGEMENT

Support of the program was provided by the Office of Coal Research on Contract Number 14-01-0001-493. The technical assistance of A. Bothe, T. Henze, R. McDonough, and R. Ruediger in planning and performing the described experiments is gratefully acknowledged.

REFERENCES

1. Kavlick, V.J., and Lee, B.S., Amer. Chem. Soc., Div. Fuel Chem., Preprints 10, (4), 131-9 (1966).

2. Curran, G.P., Struck, R.T., and Gorin, E., Amer. Chem. Soc., Div. Fuel Chem., Preprints 10, (2), C-130--C-148 (1966).

3. Lefrancois, P.A., Barclay, K.M., and Skaperdas, G.T., Amer. Chem. Soc., Div. Fuel Chem., Preprints 10, (4), 198-205 (1966).

4. Eddinger, R.T., Friedman, L.D., and Rau, E., Fuel 45, (3), 245-52 (1966).

5. Krukonis, V.J., and Schoenberg, T., Paper 5-132, 7th International Conference on Coal Science, Prague (1968).

6. Krukonis, V.J., Gannon, R.E., and Schoenberg, T., Paper to be presented at the 19th Canadian Chemical Engineering Conferencem Edmonton, Alberta, October, 1969.

7. Sharkey, A.G. Jr., Schultz, J.L., and Friedel, R.A., Coal Sciences, Adv. in Chem. Series 55, 643-644 (1966).

8. Rau, E., and Seglin, L., Fuel 43, (2), 147-57 (1964).

9. Bond, R.L., Ladner, W.R., and McConnel, G.I.T., Coal Sciences, Adv. in Chem. Series 55, 650-665 (1966).

10. Kawa, W., Graves, R.D., and Hiteshue, R.W., U.S. Bureau of Mines, Rept. Invest. 6829 (1966).

11. Kawana, Y., Makino, M., and Tatsuo Kimura, Kogyo Kagaku Zasshi, 69, (6), 1144-50 (1966).

12. Newman, J.O.H., et al, 7th International Conference on Coal Science, Prague (1968).

13. Littlewood, K., McGrath, I.A., Paper C9, 5th International Conference on Coal Science, Cheltenham (1963).

14. Rau, E., Eddinger, R.T., Fuel 43 (3), 246 (1964).

15. Wagman, et. al, J. Res. Nat. Bur. Stand., 1945, 35, p. 467.

16. Howard, Wood and Kaltenbacher, Chem. Eng. Prog. , 1961, 57 , (11) p. 50.

17. Kozlov, G.I. et. al, Int'n. Chem. Eng., 8, No. 2, April, 1968, p. 289.

18. Office of Coal Research, R.& D. Report No. 34 "AVCO Arc-Coal Process" OCR Contract No. 14-01-0001-493, April 1968.

19. O'Hara, J.B., Chem. Eng . Prog., 63, April 1967, p. 61.

20. Gladisch, H., Hydrocarbon Proc. & Pet. Ref., 41 (6), 159 (1962).

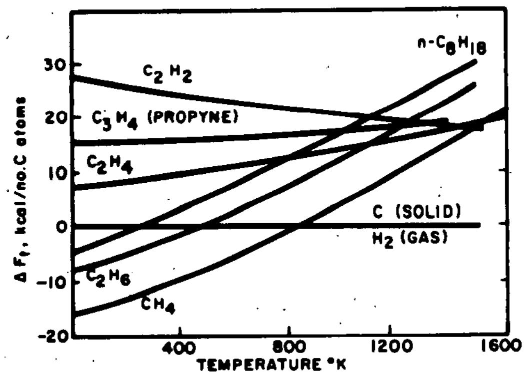

Figure 1 FREE ENERGIES OF FORMATION OF SELECTED HYDROCARBONS

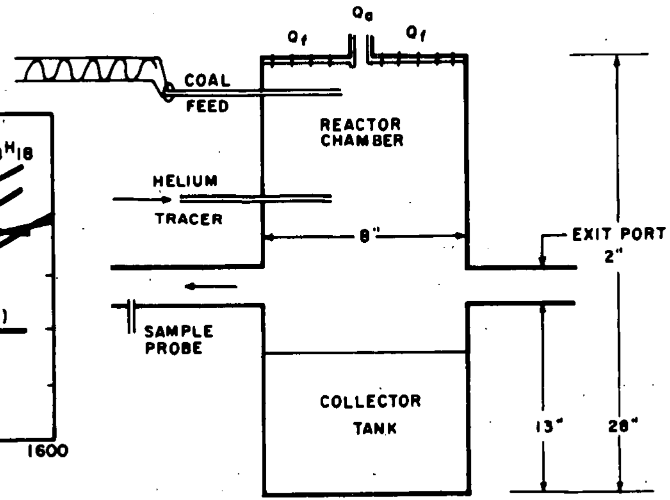

Figure 2 ARC HEATED HYDROGEN REACTOR

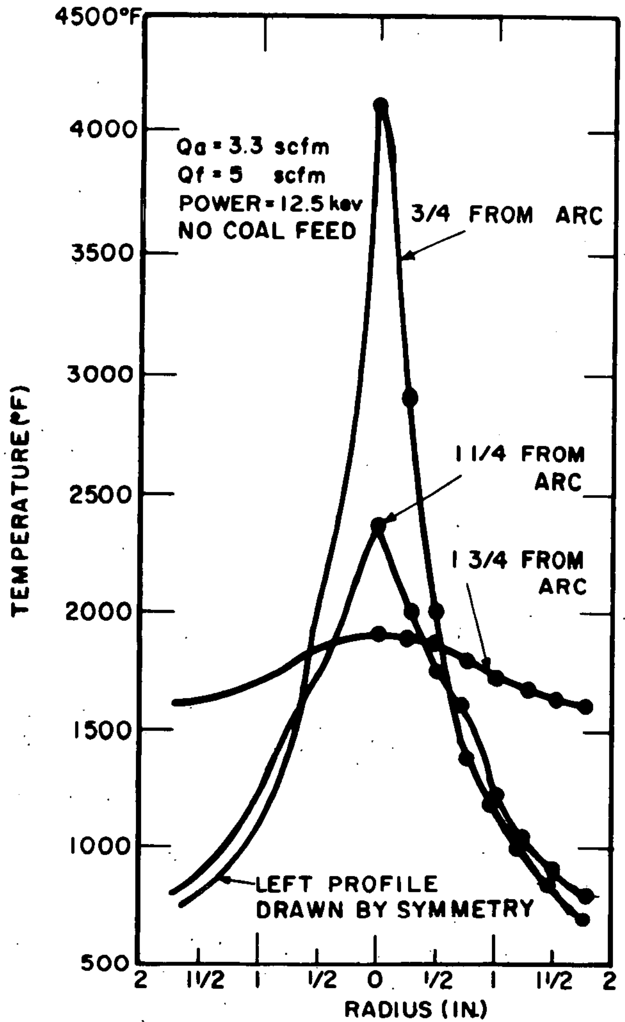

Figure 3 TEMPERATURE DISTRIBUTION IN REACTOR

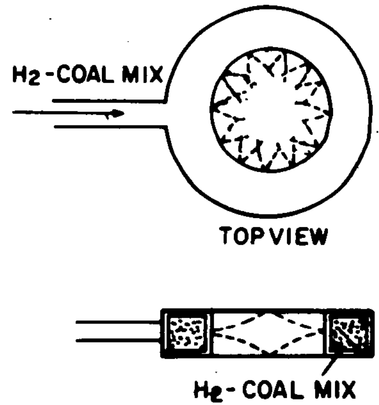

Figure 4 COAL FEED MANIFOLD

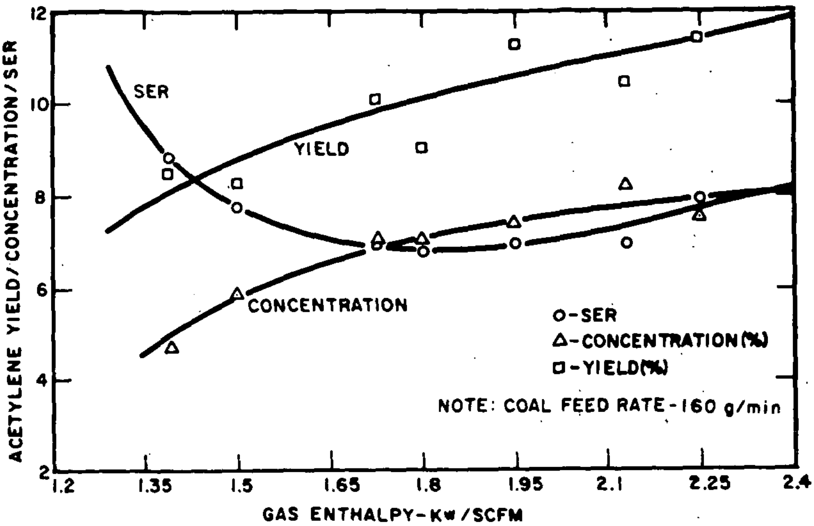

Figure 5 ACETYLENE YIELD, CONCENTRATION AND SER AS A FUNCTION OF GAS ENTHALPY

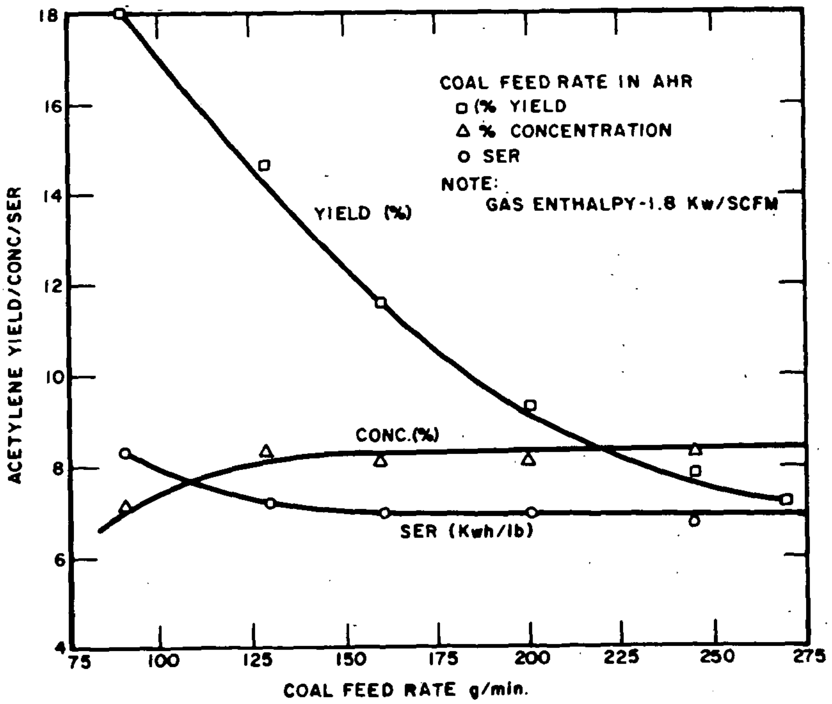

Figure 6 ACETYLENE YIELD, CONCENTRATION AND SER AS A FUNCTION OF COAL FEED RATE

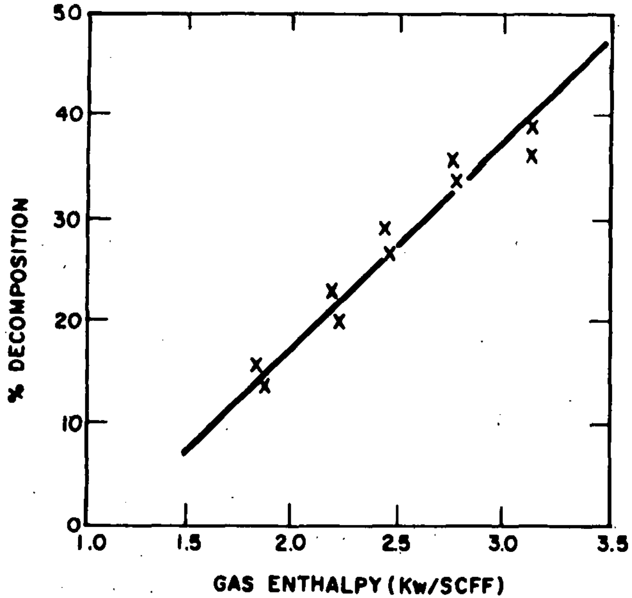

Figure 7 ACETYLENE DECOMPOSITION AS A FUNCTION OF GAS ENTHALPY

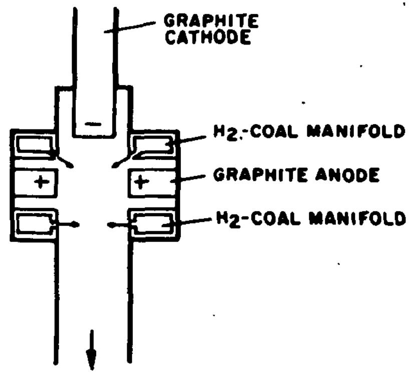

Figure 8 ARC REACTOR WITH DUAL COAL FEED